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Carbazole-Based Boron Dipyrromethenes (BODIPYs): Facile Synthesis, Structures, and Fine-Tunable Optical Properties

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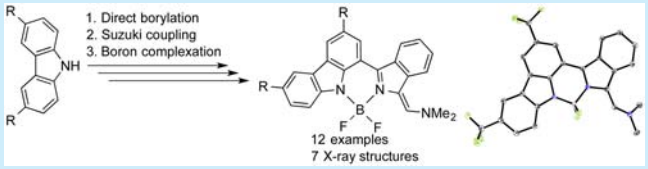
Supporting Information

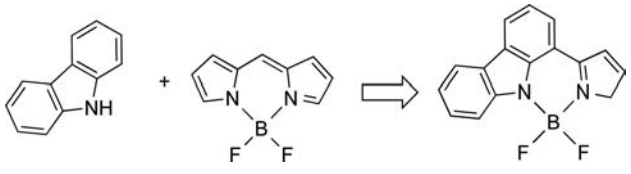
ABSTRACT: Carbazole-based BODIPYs were synthesized in three steps using an organometallic approach consisting of sequential Ir-catalyzed borylation, Suzuki–Miyaura coupling, and boron complexation. Various substituents were introduced into the carbazole moiety, and large substituent effects were confirmed by means of absorption spectroscopy, cyclic voltammetry, and DFT calculations. Dibenzocarbazoles were also converted into the corresponding BODIPYs.



Boron dipyrromethene (BODIPY) derivatives show promise as dyes because of their high extinction coefficients and fluorescent quantum yields and since they are also chemically, thermally, and photostable.[1] These properties suggest that BODIPYs will have applications in fluorescent sensors, biological labeling, photodynamic therapies, and photovoltaic cells. To date, a number of BODIPYs, including fused,[2] aza,[3] and oligomeric[4] varieties, have been developed. Such BODIPYs have often been synthesized by acid-catalyzed condensation, and their functionalization has been extensively studied. However, the design of novel BODIPY derivatives by alternative synthetic protocols has rarely been reported.

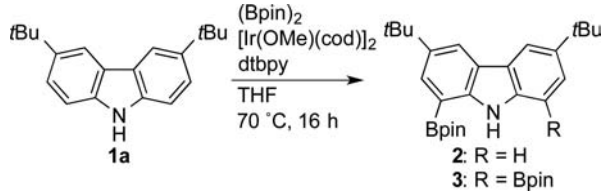
Carbazole derivatives have also been studied as potential electron conductors, catalysts, and sensors. Recently, we reported the synthesis of carbazole-based porphyrinoids[5] and found that the incorporation of carbazole units into the porphyrin core generated some interesting properties. BODIPY is known as porphyrin's little sister, and so we assessed the feasibility of incorporating a carbazole unit into a BODIPY framework (Scheme 1).[6] Herein we report the synthesis of carbazole-based BODIPYs based on an organometallic approach. In this method, a pyrrolic skeleton is attached to the 1-position of the carbazole via Ir-catalyzed borylation and Suzuki–Miyaura coupling. Boron complexation of the resulting dipyrrin affords the carbazole-based BODIPY.

Scheme 1. Schematic Representation of the Construction of a Carbazole-Based BODIPY



We decided to use Ir-catalyzed direct borylation to functionalize the 1-position of the carbazole because of the high selectivity and functionality tolerance of this method.[7] Borylation of the carbazole occurred selectively at the 1,8-positions because the NH moiety acted as a directing group.[8] Initially, we optimized the reaction of 3,6-di-*tert*-butylcarbazole (**1a**) (Scheme 2 and Table 1). Using 0.5 and 1.0 equiv of

Scheme 2. Ir-Catalyzed Borylation of Carbazole 1a (cod = 1,5-cyclooctadiene, dtbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridyl)



$(Bpin)_2$, the monoborylated carbazole **2** and the bis-borylated carbazole **3** were produced as the major product, respectively

Table 1. Ir-Catalyzed Borylation of Carbazole 1a[a]

entry	$(Bpin)_2$ (equiv)	yield (**1a**/**2**/**3**)[b]
1	0.50	30/62/8
2	0.60	26/62/12
3	0.65	14/65/21
4	0.75	11/61/28
5	1.0	13/20/67
6	2.0	10/–[c]/90(79[d])

[a]Conditions: **1a** (1.0 mmol), $[Ir(OMe)(cod)]_2$ (10 μmol), dtbpy (20 μmol), and THF (1.0 mL). [b]NMR yield. [c]Not detected. [d]Isolated yield after recrystallization.

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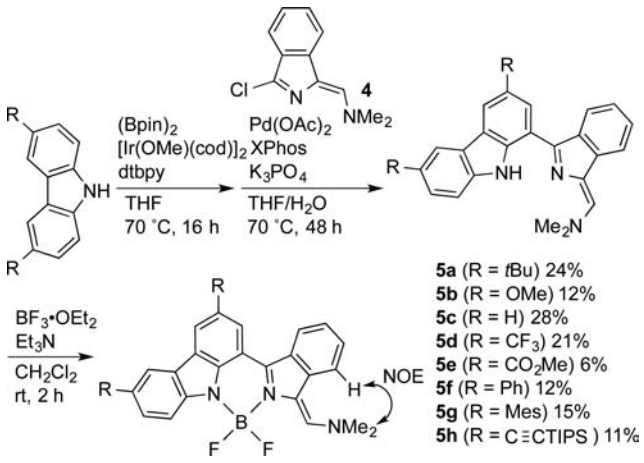
(entries 1 and 5). Further increases in the amount of $(Bpin)_2$ selectively provided **3** in 79% isolated yield (entry 6). To maximize the yield of **2**, we carefully optimized the reaction conditions while using from 0.5 to 1.0 equiv of $(Bpin)_2$. As a result, 0.65 equiv was found to be the optimal amount (entries 2–4).

Following the borylation of **1a**, the carbazole-based BODIPY was synthesized by the Suzuki–Miyaura coupling reaction and subsequent boron complexation (Scheme 3). We selected 1-(3-chloro-1*H*-isoindol-1-ylidene)-*N*,*N*-dimethylmethanamine (**4**) as the coupling partner because **4** contains a benzo fusion moiety and is easily prepared.[9] Following the borylation (Table 1, entry 3), a mixture of **1a**, **2**, and **3** was subjected to the Suzuki–Miyaura coupling reaction with **4** using $Pd(OAc)_2$ and XPhos as the catalytic system.[10] The subsequent complexation with $BF_3{\cdot}OEt_2$ afforded the carbazole-based BODIPY **5a** from **1a** in 24% yield. The high-resolution mass spectrum of **5a** exhibited a parent ion peak at an *m*/*z* value of 497.2833 (calcd for $C_{31}H_{34}N_3BF_2$ 497.2814 $[M]^+$). Various substituents, including electron-donating and -withdrawing, aryl and ethynyl, groups were subsequently attached to the 3,6-positions of the carbazole moiety. Importantly, nonsubstituted **5c** and phenyl-substituted **5f** were also obtained in acceptable yields, indicating that selective borylation occurred. Single crystals of **5b**, **5c**, **5d**, **5f**, and **5g** were obtained by the slow diffusion of methanol vapor into their dichloromethane or toluene solutions. The resulting X-ray crystal structures unambiguously demonstrated BODIPY skeletons (Figure 1 and Figures S17–23 in Supporting Information), in which the dimethylamino group is oriented outside of the structure. The ^1H–^1H NOESY spectra of these compounds confirmed a correlation between the NMe_2 moiety and the benzo-proton, which also supports the *E*-conformer (see Figure S2). Because **4** was determined to exist as the *Z*-conformer[9b] and the excess amount of **4** was recovered without isomerization after the Suzuki–Miyaura reaction, this isomerization is thought to have occurred during the boron complexation, likely due to the repulsion between the dimethylamino group and the BF_2 moiety.

The UV/vis absorption spectra of these compounds are shown in Figure 2, and the corresponding data are summarized in Table 2. All the compounds show three bands at approximately 300, 400, and 500 nm, which were effectively shifted by the substituents. Introduction of electron-withdrawing groups, and of electron-donating groups or aryl groups, generated blue and red shifts, respectively, indicating efficient substituent effects. The fluorescence spectra of the BODIPYs were also perturbed by the substituents, although the fluorescence quantum yields were very low. As compared to general BODIPYs, these dyes show broad spectra and a large Stokes shift value.[11]

The oxidation and reduction potentials of the BODIPYs were measured to examine the effects of the substituents on the π-networks of the BODIPY frameworks (Table 3 and Figure S15). Cyclic voltammetry (CV) showed one reduction wave at ca. −1.8 V regardless of the substituents and two oxidation waves that were dependent on the substituents. Those compounds having electron-donating and -withdrawing groups exhibited lower and higher oxidation potentials, respectively. The HOMO–LUMO gaps of the molecules with electron-donating, aryl and ethynyl groups were smaller, whereas the compounds with electron-withdrawing groups had larger gaps, which is in good agreement with the optical gap data obtained from absorption spectroscopy and also with the calculated gaps.

Scheme 3. Synthesis of 5a–5h



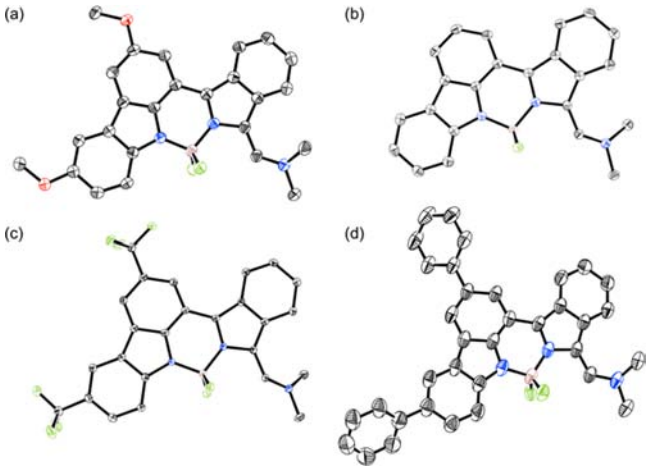


Figure 1. X-ray crystal structures of (a) **5b**, (b) **5c**, (c) **5d**, and (d) **5f**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids are drawn at the 50% probability level.

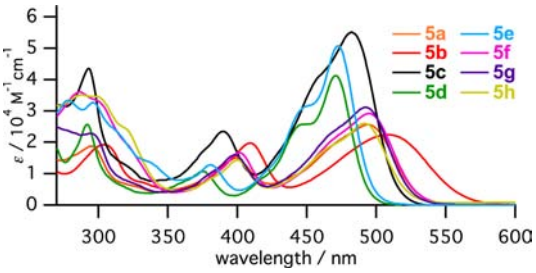


Figure 2. UV/vis absorption spectra of **5a–5h** in CH_2Cl_2.

Table 2. Photophysical Data in CH_2Cl_2

compd	λ_A (nm)	λ_F (nm)	$\Delta\nu_{St}$ (cm^{-1})
5a	292, 398, 493	561	2460
5b	304, 409, 508	650	4300
5c	292, 390, 482	528	1810
5d	291, 375, 448, 475	508	1370
5e	278, 296, 381, 472	519	1920
5f	287, 401, 495	559	2310
5g	293, 398, 492	555	2310
5h	289, 400, 492	571	2810

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Table 3. Electrochemical Results[a]

compd	E_{red} (V)	E_{ox} (V)	ΔE_{CV}	ΔE_{opt}	ΔE_{DFT}[b]
5a	−1.850	0.429, 0.770	2.279	2.52	2.76
5b	−1.823	0.302, 0.717	2.125	2.44	2.57
5c	−1.849	0.485, 0.663	2.334	2.57	2.86
5d	−1.739	0.681, 1.044	2.421	2.61	3.02
5e	−1.760	0.640, 0.940	2.400	2.63	3.00
5f	−1.809	0.462, 0.848	2.271	2.51	2.72
5g	−1.813	0.472, 0.808	2.285	2.52	2.67
5h	−1.779	0.536, 0.861	2.315	2.52	2.73

[a]Determined by cyclic voltammetry. Solvent: CH_2Cl_2. Supporting electrolyte: Bu_4NPF_6 (0.10 M). Reference electrode: Ag/Ag^+. Scan rate: 0.1 V/s. [b]Calculated at the B3LYP/6-31G* level.

Thus, efficient substituent effects were also observed in the electrochemical studies.

In order to better understand the electronic and electrochemical properties, DFT calculations were performed.[12] The HOMOs and LUMOs of **5b**, **5c**, and **5d** are shown in Figure 3.

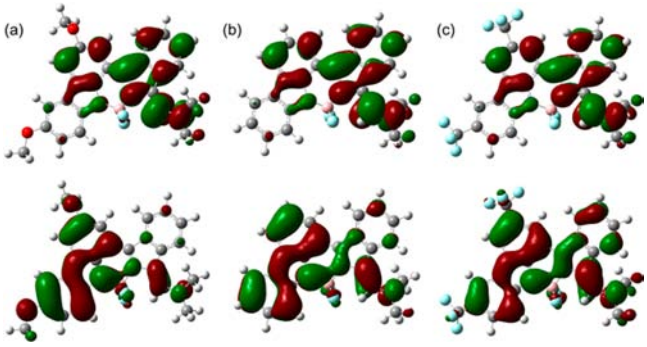


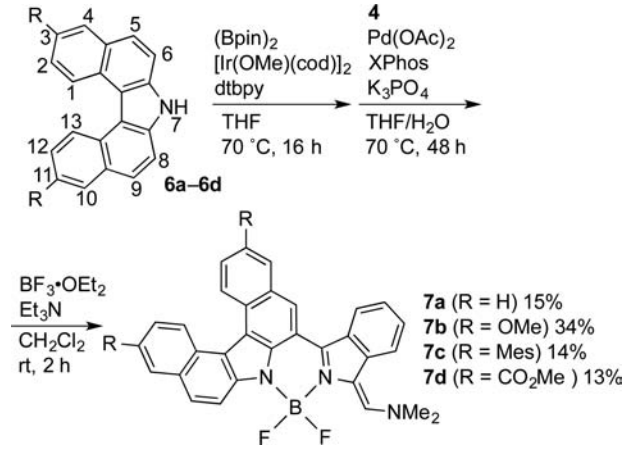
Figure 3. HOMO (bottom) and LUMO (top) of (a) **5b**, (b) **5c**, and (c) **5d** calculated at the B3LYP/6-31G* level.

The HOMOs exhibit large electronic coefficients on the carbazole moiety, especially in the case of **5b**. In contrast, the LUMOs are almost the same and exhibit electronic coefficients primarily on the isoindole moieties. These results strongly suggest that the observed fluorescence quenching resulted from intramolecular charge transfer (ICT) from the carbazole moiety to the isoindole moiety.[13] TD DFT calculations were also performed to assign the absorption bands: The bands at 500 and 400 nm are related to the transition from the HOMO to the LUMO and that from the HOMO−2 to the LUMO, respectively (Figure S14).

Finally, we applied this reaction to dibenzocarbazole derivatives **6a**−**6d** (Scheme 4) and found that these compounds also underwent conversion to the corresponding BODIPYs **7a**−**7d** by a similar process. The structures of **7a** and **7c** were confirmed by X-ray diffraction analyses (Figure 4). Although the HOMO and LUMO of dibenzocarbazole exhibit large electronic coefficients at the 5,9-positions (see Figure S16) and these positions are reactive,[14] the Ir-catalyzed borylation took place selectively at the 6-position due to the steric properties and the directing group. Therefore, this method was found to be suitable for functionalization at the 6,8-positions of the dibenzocarbazoles. The UV/vis absorption spectra of **7a**−**7d** show similar broad bands in the visible region, exhibiting slight substituent effects (Figure S14).

In summary, we have synthesized novel BODIPY dyes based on carbazole skeletons through sequential Ir-catalyzed

Scheme 4. Synthesis of 7a−7d



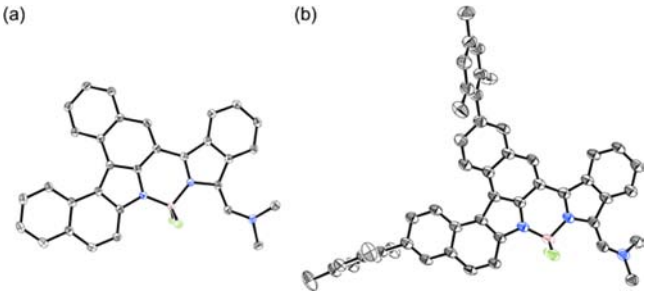


Figure 4. X-ray crystal structures of (a) **7a** and (b) **7c**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids are drawn at the 50% probability level.

borylation, Suzuki−Miyaura coupling, and boron complexation. The structures of these compounds have been elucidated by NMR and X-ray diffraction analyses. Various substituents were attached to the 3,6-positions of the carbazole moiety, and the resulting substituent effects were confirmed by means of UV/vis absorption spectroscopy, CV, and DFT calculations. We were also able to apply Ir-catalyzed borylation to dibenzocarbazoles and consequently succeeded in the synthesis of the corresponding BODIPYs. Further investigations of the development of carbazole-based materials are currently underway.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, compound data, and crystallographic data in CIF format. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b01363.

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Notes

The authors declare no competing financial interest.

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